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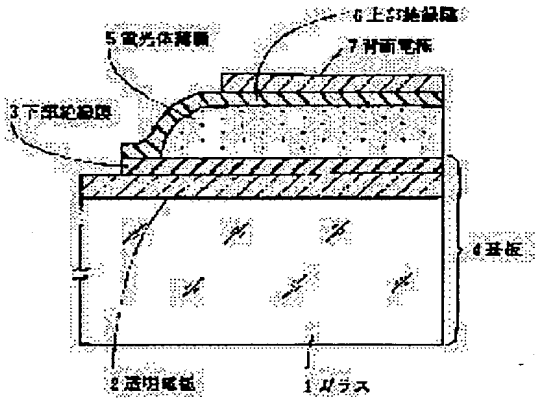
(54) PHOSPHOR THIN FILM AND MANUFACTURE THEREOF AND THIN FILM EL PANEL

(57)Abstract:
PURPOSE: To provide a wide range multicolor EL from red to blue that does not need a filter.
CONSTITUTION: A transparent electrode 2 and a lower insulating film 3 are formed on a glass sheet 1 in this order to form a substrate 4 for EL element. A phosphor thin film 5 is formed by 600-800nm on the substrate 4. After an upper insulating film 6 is formed on the phosphor thin film 5, a back plate 7 is formed thereon to form a thin film EL element. The phosphor thin film 5 is a phosphor thin film primarily consisting of a compound expressed by a constitutional formula of AB2C4:Re, where A is at least one element chosen among a group of Mg, Ca, Sr, Ba, Eu and Yb, B is at least one element chosen among a group of Al, Ga and In, C is at least one element chosen between S or Se, and Re is a rare earth additive.



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(56)参考文献　特開　平４－121992（ＪＰ，Ａ）
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最終頁に続く

(54)【発明の名称】　蛍光体薄膜とこれを用いた薄膜ＥＬパネル

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(57)【特許請求の範囲】

【請求項１】　AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜であって、前記ＡがＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素であり、前記ＢがＩｎおよびＡｌから選ばれた少なくとも１つの元素とＧａとを組み合わせた複合元素であり、前記ＣがＳおよびＳｅから選ばれた少なくとも一つの元素であり、前記Ｒｅが希土類の添加物であることを特徴とする蛍光体薄膜。

【請求項２】　AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜であって、前記ＡがＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素であり、前記ＢがＩｎおよびＡｌから選ばれた少なくとも一つの元素であり、前記ＣがＳおよびＳｅから選ばれた少なくとも一つの元素であり、前記Ｒｅが希土類の添加物であることを特徴とする蛍光体薄膜。

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【請求項３】　ＲｅがＥｕおよびＣｅから選ばれた少なくとも一つの元素である請求項１および２記載の蛍光体薄膜。

【請求項４】　ＡがＳｒであり、ＢがＩｎであり、ＣがＳであり、ＲｅがＥｕであることを特徴とする請求項３記載の蛍光体薄膜。

【請求項５】　請求項１～４記載の蛍光体薄膜を有する薄膜ＥＬパネル。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】この発明は、薄型で表示の視認性が優れ、ＯＡ機器等の端末ディスプレイとして最適であり、多色表示薄膜ＥＬパネルへ応用できる薄膜ＥＬパネ

ルの蛍光体薄膜とこれを用いた薄膜ＥＬパネルに関するものである。

【０００２】

【従来の技術】近年、薄膜ＥＬ素子の蛍光体薄膜の母体材料として、硫化亜鉛、硫化カルシウム、硫化ストロンチウム、セレン化亜鉛、セレン化ストロンチウム等のII－VI族化合物半導体が、また母体材料に添加する発光中心となる元素として、マンガンやテルビウム、サマリウム、ツリウム、ユーロピウム、セリウム等の希土類元素が知られている。多色表示薄膜ＥＬパネル、なかでも、フルカラー表示が可能なＥＬパネルを作製するためには、蛍光体薄膜から、高輝度かつ高色純度の赤、緑、青の３種類の発光を得る必要がある。ＺｎＳ：Ｍｎ蛍光体薄膜からの黄橙色光の赤色成分をＣｄＳＳｅや有機化合物の赤色フィルタを用いて分離することにより得られる赤色発光、ならびに、ＺｎＳ：Ｍｎ蛍光体薄膜からの黄橙色光の緑色成分を有機化合物の緑色フィルタを用いて分離することにより得られる緑色発光やＺｎＳ：Ｔｂ蛍光体薄膜からの緑色発光が、現在、多色表示薄膜ＥＬパネルに用いられている。青色発光としては、ＳｒＳ：Ｃｅ蛍光体薄膜から得られる高輝度の青緑色発光が知られている。青色フィルタと組み合わせることにより、色純度の良い青色発光を得ることができる。

【０００３】

【発明が解決しようとする課題】しかしながら、蛍光体の母体材料や発光中心材料が有する化学的あるいは物理的な性質が、個々の材料により異なっているために、蛍光体薄膜の種類によって、高い輝度を得るための製膜方法が異なるために、多色薄膜ＥＬパネルの製造工程が、複数種類の製膜装置が必要になるなどの理由により、一層複雑になり、パネルの製造コストが高くなる問題があった。例えば、前記ＺｎＳ：Ｍｎ蛍光体薄膜は、抵抗線加熱蒸着法、電子ビーム蒸着法、原子層エピタキシャル（ＡＬＥ）法を用いて製膜することにより、高い輝度が得られている。また、ＺｎＳ：Ｔｂ蛍光体薄膜は高周波スパッタ法、そして、ＳｒＳ：Ｃｅ蛍光体薄膜は電子ビーム蒸着法を用いて製膜することにより高い輝度が得られている。上記問題を解決するために、同一の製膜手法や製膜装置を用いて高い輝度を得ることが可能となる、化学的あるいは物理的な性質が類似した、蛍光体母体材料や発光中心材料が求められていた。

【０００４】また、従来の前記蛍光体薄膜（ＺｎＳ：Ｍｎ、ＺｎＳ：Ｔｂ、ＳｒＳ：Ｃｅ）を用いて、多色薄膜ＥＬパネルを作製した場合、赤、緑、青の発光を得るために、ＣｄＳＳｅや有機化合物のフィルタを必要とする場合が多く、多色薄膜ＥＬパネルの製造工程がより複雑になる問題や、フィルタを透過することにより透過前の輝度の１０～６０％にまで輝度が低下して、パネルの画像が暗くなる問題があった。上記問題を解決するために、フィルタを用いなくとも色純度の良好な赤、緑、青の発光を得ることができる蛍光体薄膜が求められていた。

【０００５】この発明は、フィルタを必要としない、赤から青までの広範囲にわたる多色ＥＬを得ることを目的とする。また、この発明は、多色表示薄膜ＥＬパネルの製造工程を簡略化し、多色表示薄膜ＥＬパネルの製造コストを低減することを目的とする。

【０００６】

【課題を解決するための手段】上記目的を達成するために、本発明の蛍光体薄膜は、ＡＢ2 Ｃ4 ：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜のＡがＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素になるようにし、ＢがＩｎおよびＡｌから選ばれた少なくとも１つの元素とＧａとを組み合わせた複合元素になるようにし、ＣがＳおよびＳｅから選ばれた少なくとも一つの元素になるようにし、Ｒｅが希土類の添加物になるようにする。

【０００７】また、本発明の蛍光体薄膜は、ＡＢ2 Ｃ4 ：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜であって、ＡがＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素になるようにし、ＢがＩｎおよびＡｌから選ばれた少なくとも一つの元素になるようにし、ＣがＳおよびＳｅから選ばれた少なくとも一つの元素になるようにし、Ｒｅが希土類の添加物になるようにする。

【０００８】希土類の添加物はＥｕおよびＣｅから選ばれた少なくとも一つの元素にするのがよい。なお、赤色に発光する蛍光体薄膜を得るには、ＡをＳｒ、ＢをＩｎ、ＣをＳ、ＲｅをＥｕにする。また、蛍光体薄膜中の希土類元素の上記Ａに対する含有量は０．１～１０原子％になるようにする。

【０００９】さらに本発明の薄膜ＥＬパネルは、上記ＡＢ2 Ｃ4 ：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜を用いて構成する。

【００１０】

【作用】この発明によれば、蛍光体薄膜が赤から青までの広範囲にわたる様々な色の発光を放射するようになる。とりわけ、ＳｒＩｎ2 Ｓ4 ：Ｅｕ蛍光体薄膜は色純度の良好な赤色発光を、Ｓｒ（Ｉｎ，Ｇａ）２Ｓ4 ：Ｅｕ蛍光体薄膜は色純度の良好な緑色発光を、ＢａＡｌ2 Ｓ4 ：Ｅｕ蛍光体薄膜やＳｒ（Ｉｎ，Ｇａ）２Ｓ4：Ｃｅ蛍光体薄膜は色純度の良好な青色発光を放射するようになる。

【００１１】なお、蛍光体薄膜の添加物である希土類は、化合物の中で希土類イオンとして存在し、発光中心として働く。この場合、希土類イオンの固有の性質に起因した色の発光を示すようになる。さらに、この発明によれば、薄膜ＥＬパネルが赤から青までの広範囲にわたる様々な色の発光を放射するようになる。とりわけ、ＳｒＩｎ2 Ｓ4 ：Ｅｕ蛍光体薄膜を用いて薄膜ＥＬパネル

を構成することにより、薄膜ＥＬパネルが輝度の高い赤色発光を放射するようになる。

【００１２】

【実施例】（第１の実施例）

以下に、この発明の第１の実施例について図面を参照しながら説明する。図１はこの発明を適用できる薄膜ＥＬパネルの断面図である。ガラス１上に、錫を添加した酸化インジウム（ＩＴＯ）の透明電極２と、酸窒化珪素（ＳｉＯＮ）の下部絶縁膜３を高周波スパッタ法を用いて順次堆積させてＥＬパネル用の基板４とした。基板４上に、蛍光体薄膜５を６００～８００ｎｍ形成した。蛍光体薄膜５上に、タンタル酸バリウム（$BaTa_2O_x$；ｘは約６）の上部絶縁膜６を高周波スパッタ法を用いて堆積させた後、アルミニウム（Ａｌ）の背面電極７を電子線加熱蒸着法で堆積して、薄膜ＥＬパネルとした。ＩＴＯの透明電極２とＡｌの背面電極７との間に、周波数１ｋＨｚの交流電圧を印加して、薄膜ＥＬパネルを駆動した。

【００１３】以下、第１の実施例の蛍光体薄膜の製造方法を説明する。この第１の実施例の蛍光体薄膜は、発光中心となる希土類元素がＥｕである$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体薄膜である。図２はこの第１の実施例の蛍光体薄膜の製造装置である高周波スパッタ装置の概念図である。

【００１４】スパッターゲット８として、$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体粉末を用いた。発光中心となる希土類の添加物であるＥｕの添加量は、５原子％、すなわち、ｘ＝０．０５とした。Ｉｎ：Ｇａの比率は５：９５とした。Ａｒ＋５％H_2S混合ガスをスパッタガス９とした。１０はガス導入バルブ、１１は高周波電源、１２は絶縁体、１３は真空槽、１４は主バルブ、１５は油拡散ポンプ、１６は油回転ポンプである。基板温度３００～６００℃、ガス圧５Ｐａ、高周波電力密度３．８Ｗ／ｃｍ^{2}のスパッタ条件のもとで、スパッタ速度、約１０ｎｍ／ｍｉｎが得られた。上記スパッタ条件のもとで、基板４上に、Ｓｒ－Ｅｕ－Ｉｎ－Ｇａ－Ｓからなる薄膜を製造した後、真空中で６５０℃１時間の熱処理を行うことにより、優れたＥＬ特性を示す$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体薄膜を製造することができた。

【００１５】図３は蛍光体薄膜のＸ線回折パターンを示す図である。比較のために、従来例として、スパッタガスをＡｒとして製膜した薄膜のＸ線回折パターンも同図に示した。スパッタガスがＡｒガスである従来からのスパッタ法に代えて、この第１の実施例では、Ｓを有する水素化物のガスであるH_2Sを５％スパッタガス中に含むＡｒ＋H_2S混合ガスをスパッタガスとする反応性スパッタ法とすることによって、Ｘ線回折パターンに数本のピークを認めることができた。このことは、この第１の実施例の蛍光体薄膜の製造方法によって、結晶化した

薄膜が得られることを示しており、さらに詳しくは、Ａｒ＋H_2S混合ガスをスパッタガスとする反応性スパッタ法とすることによって、高性能の蛍光体薄膜母体が製造できたことを示している。

【００１６】図４は蛍光体薄膜のＥＬ特性を示す図である。電圧に対する輝度の変化を示している。比較のために、従来例として、スパッタガスをＡｒとして製膜した薄膜のＥＬ特性も同図に示した。図４に示した第２の実施例のＥＬ特性は、後で説明する。スパッタガスがＡｒガスである従来からのスパッタ法に代えて、この第１の実施例では、Ｓを有する水素化物のガスであるH_2Sを５％スパッタガス中に含むＡｒ＋H_2S混合ガスをスパッタガスとする反応性スパッタ法とすることによって、高いＥＬ輝度を得ることができた。このことは、この第１の実施例の蛍光体薄膜の製造方法によって、高性能の蛍光体薄膜が製造できたことを示している。スパッタガス中のH_2Sは、蛍光体薄膜が成長する最中に、蛍光体薄膜からのＳ成分の再蒸発を防止する役割を担うと考えられる。

【００１７】図５は蛍光体薄膜のＥＬスペクトルを示す図である。第２の実施例のＥＬスペクトルは後で説明する。発光のピーク波長は約５２６ｎｍであり、スペクトルの半値幅は約４７ｎｍであった。このことは、この第１の実施例の蛍光体薄膜の製造方法によって製造した蛍光体薄膜が、緑色発光を示す$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体薄膜であることを示している。

【００１８】以上説明したように、$Sr(In,Ga)_2S_4$：Ｅｕの構造式で表わされる蛍光体薄膜を、Ｓを有する水素化物であるH_2Sガスをスパッタガス中に含む反応性スパッタ法により形成することにより、高性能の$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体薄膜を製造することができ、高い輝度の薄膜ＥＬを得ることができた。

【００１９】この第１の実施例では、蛍光体薄膜材料を、緑色発光$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体とした場合について説明したが、Ｓｒに代えてＭｇ、Ｃａ、Ｂａ、Ｅｕ、Ｙｂとしたり、Ｅｕ希土類元素に代えてＣｅやＰｒ等の希土類元素としたり、Ｇａに代えてＡｌやＩｎとしたりした、$Sr(In,Ga)_2S_4$：Ｅｕ以外の蛍光体薄膜でも、薄膜ＥＬを観察することができた。希土類の添加物の中では、ＥｕとＣｅが高い輝度を示し、とりわけ、赤色発光$SrIn_2S_4$：Ｅｕ、緑色発光$Sr(In,Ga)_2S_4$：Ｅｕ蛍光体薄膜の場合に高輝度ＥＬを得ることができた。また、$Sr(In,Ga)_2S_4$：Ｃｅや$BaAl_2S_4$：Ｅｕ蛍光体薄膜の場合には、色純度に優れた青色ＥＬ発光素子を得ることができた。

【００２０】以上説明したように、AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜から、可視域全域にわたる薄膜ＥＬを実現することができ

た。なお、AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜において、Ａ、Ｂ、Ｃ、Ｒｅは、単一の元素に限定されるものではない。例えば、$(Sr_{1-x}Ca_x)(Ga_{1-y}In_y)_2(S_{1-z}Se_z)_4$：Ｅｕ，Ｃｅのように、Ａ、Ｂ、Ｃ、を構成する元素を複数にしてもよいし、希土類元素を複数種類添加してもよいことはいうまでもない。

【００２１】また、この実施例では、Ａｒ＋H_2S混合ガスをスパッタガスとした反応性スパッタ法により、緑色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ蛍光体薄膜を製膜した場合について説明したが、例えば、Ｓｒ（Ｉｎ，Ｇａ）２Ｓｅ４：Ｅｕ蛍光体薄膜の場合では、Ａｒ＋H_2Se混合ガスをスパッタガスとし、スパッターゲットを$SrGa_2Se_4$：Ｅｕ蛍光体粉末とした反応性スパッタ法により、高輝度ＥＬを示す蛍光体薄膜を製膜できたし、$Sr(In,Ga)_2(S_{1-x}Se_x)_4$：Ｅｕ蛍光体薄膜の場合では、Ａｒ＋$H_2Se$混合ガスをスパッタガスとし、スパッターゲットを$SrGa_2S_4$：Ｅｕ蛍光体粉末とした反応性スパッタ法により製膜できた。

【００２２】さらに、この第１の実施例では、緑色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ蛍光体粉末をスパッターゲットとした場合を説明したが、粉末ターゲットに代えてセラミクスターゲットを用いても、粉末ターゲットの場合と同様の優れたＥＬ特性を示す蛍光体薄膜を得ることができた。セラミクスターゲットの方が、より再現性よく蛍光体薄膜を製膜できた。

【００２３】この第１の実施例は、AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜において、Ｃを構成する元素を有する水素化物のガスをスパッタガス中に含む反応性スパッタ法により蛍光体薄膜を形成することを特徴とするものでもある。したがって、スパッタガス中に、Ｃを構成する元素を有する水素化物のガスが含まれておればよく、スパッターゲットの形態や形状、また、ガスの混合量やガスの種類について制限されるものではない。例えば、Ａｒ＋H_2S混合ガスに代えて、Ａｒ＋Ｈｅ＋H_2S＋H_2Se混合ガスのような複数種類のガスの混合ガスを用いても良いし、Ｃを構成する元素を有する水素化物のガスの混合量が５％でなくてもよい。

【００２４】（第２の実施例）

つぎに、AB_2C_4：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜において、Ａ、Ｂ、Ｃ、Ｒｅを構成する各元素を一種類以上有する複数の蒸気ガスを、独立に制御して基板表面に供給する蛍光体薄膜の製造方法について説明する。すなわち、第２の実施例である発光中心となる希土類の添加物がＥｕの赤色発光$SrIn_2S_4$：Ｅｕ蛍光体薄膜の製造方法を説明する。

【００２５】図６はこの第２の実施例の蛍光体薄膜の製造装置の概念図である。Ａ、Ｂ、Ｃ、Ｒｅを構成する各金属元素を有する複数の蒸気ガスを、各々、Ｓｒ金属蒸気ガス、Ｅｕのハロゲン化物である$EuCl_3$化合物蒸気ガス、Ｉｎ金属蒸気ガス、H_2Sガスとした反応性蒸着法により第２の実施例の蛍光体薄膜の製造を行う。

【００２６】図６において、まず、高真空槽１３に設置した基板４を６００℃に加熱し、1×10^{-6}Ｐａ以下まで高真空装置を排気した。基板４の表面に所定量のH_2Sを供給するために、1×10^{-2}Ｐａの圧力になるようガス導入バルブ１０を操作して、H_2Sガスボンベ１７からH_2Sガスを高真空装置内に導入した。つぎに、真空中に設置された、Ｓｒ金属１８、Ｉｎ金属１９、$EuCl_3$化合物粉末２０を、個別に加熱してガス化し、基板４の表面に供給した。Ｓｒ金属を５００～６００℃、Ｉｎ金属を４００～９００℃、$EuCl_3$化合物粉末を５００～８００℃に保つことにより、Ｓｒ－Ｅｕ－Ｉｎ－Ｓからなる薄膜を製造した。薄膜形成後、真空中で６５０℃１時間の熱処理を行うことにより、優れたＥＬ特性を示す、赤色発光$SrIn_2S_4$：Ｅｕ蛍光体薄膜を製造することができた。

【００２７】第２の実施例の$SrIn_2S_4$：Ｅｕ蛍光体薄膜のＥＬ特性を図４に示す。反応性スパッタ法で製膜した第１の実施例の緑色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ蛍光体薄膜の場合と比較するために図４中に示したが、この反応性蒸着法によっても高いＥＬ輝度を実現できることがわかる。図５に第２の実施例の蛍光体薄膜のＥＬスペクトルを示す。反応性スパッタ法で製膜した第１の実施例の緑色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ蛍光体薄膜の場合と比較するために、図５中に示した。発光のピーク波長は約６３０ｎｍであり、スペクトルの半値幅は約６５ｎｍであった。このことは、この蛍光体薄膜の製造方法によって製造した第２の実施例の蛍光体薄膜が、赤色発光を示す$SrIn_2S_4$：Ｅｕ蛍光体薄膜であることを示している。

【００２８】以上説明したように、$SrIn_2S_4$：Ｅｕの構造式で表わされる蛍光体薄膜を、Ｓｒ金属蒸気ガス、$EuCl_3$化合物蒸気ガス、Ｉｎ金属蒸気ガス、H_2Sガスを独立に制御して基板表面に供給して蛍光体薄膜を形成する反応性蒸着法により形成することにより、高性能の$SrIn_2S_4$：Ｅｕ蛍光体薄膜を製造することができ、高い輝度の薄膜ＥＬを得ることができた。

【００２９】この第２の実施例では、Ａ、Ｂ、Ｃ、Ｒｅを構成する各元素を一種類以上有する複数の蒸気ガスを、各々、Ｓｒ金属蒸気ガス、$EuCl_3$化合物蒸気ガス、Ｉｎ金属蒸気ガス、H_2Sガスとして基板表面に供給する場合について説明したが、H_2Sガスの代わりに、固体硫黄を加熱してガス化させた硫黄を供給しても、硫化水素ガスを用いたときと変わらない優れた品質の蛍光体薄膜を形成することができたし、$EuCl_3$化合物粉末の代わりに、金属Ｅｕを加熱してガス化させても、蛍光体薄膜を形成することができた。また、Ｓｒ金

属の代わりに、ＳｒＣｌ$_2$ 化合物粉末を加熱してガス化させても、蛍光体薄膜を形成することができたし、Ｉｎ金属の代わりに、ＩｎＣｌ$_3$ 化合物粉末を加熱してガス化させても、蛍光体薄膜を形成することができた。

【００３０】このことは、個別にガス化された、ＡとＢとＣとＲｅとを構成する各々の金属蒸気を、基板表面に供給する、ＭＢＥ法や、個別にガス化された、ＡとＢとＲｅのハロゲン化物の蒸気と、Ｃを構成する元素を有する水素化物のガスとを、基板表面に供給する、ハロゲン輸送ＣＶＤ法、さらには、複数の蒸気ガスを、基板表面に交互に供給するＡＬＥ法（別称：間欠ＣＶＤ法）でも、蛍光体薄膜が製造できることを示している。

【００３１】また、この第２の実施例では、Ａ、Ｂ、Ｃ、Ｒｅを構成する各元素を一種類以上有する複数の蒸気ガスを、各々、Ｓｒ金属蒸気ガス、ＥｕＣｌ$_3$ 化合物蒸気ガス、Ｉｎ金属蒸気ガス、H_2 Ｓガスとして、赤色発光ＳｒＩｎ$_2$ Ｓ$_4$ ：Ｅｕ蛍光体薄膜を製膜した場合について説明したが、Ｉｎ金属蒸気ガスに加えて、Ｇａ金属蒸気ガスを基板表面に供給することにより、緑色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ蛍光体薄膜が製膜できた。また、Ｓｒ金属蒸気ガス、ＣｅＣｌ$_3$ 化合物蒸気ガス、Ｉｎ蒸気ガス、Ｇａ金属蒸気ガス、H_2 Ｓガスを制御して基板表面に供給することにより、青色発光Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｃｅ蛍光体薄膜も製膜できた。

【００３２】第２の実施例は、この蛍光体薄膜の製造方法によれば、多種類にわたるこの発明の蛍光体薄膜が製膜できることを示し、赤、緑、青のこの発明の蛍光体薄膜が、一つの装置で製膜できることも示し、低コストの多色表示薄膜ＥＬパネルが製造できることを示している。第２の実施例は、Ａ、Ｂ、Ｃ、Ｒｅを構成する各元素を一種類以上有する複数の蒸気ガスを、独立に制御して基板表面に供給することを特徴とする蛍光体薄膜の製造方法に関するものである。したがって、Ａ、Ｂ、Ｃ、Ｒｅを構成する各元素を一種類以上有する複数の蒸気ガスを、独立に制御して基板表面に供給して蛍光体薄膜が製造されておればよく、各蒸気ガスの種類やガスの供給方法について制限されるものではない。蒸気ガスを供給する際の雰囲気圧力も制限されるものではない。

【００３３】（第３の実施例）

つぎに、ＡＢ$_2$ Ｃ$_4$ ：Ｒｅの構造式で表わされる化合物を主体とする蛍光体薄膜を、複数種類有する薄膜ＥＬパネルについて説明する。第３の実施例として、赤色ＳｒＩｎ$_2$ Ｓ$_4$ ：Ｅｕ、緑色Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕ、青色Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｃｅ蛍光体薄膜を有する多色表示薄膜ＥＬパネルを図７に示す。図７において、ストライプ状に加工した赤色蛍光体薄膜２１、緑色蛍光体薄膜２２、青色蛍光体薄膜２３を基板４上に並列に配置している。

【００３４】透明電極２と下部絶縁層３とが透明であるために、蛍光体薄膜からの赤、緑、青の発光を、ガラス１を通して直接観察することができた。フィルタを用いていないため、また、蛍光体薄膜が同一の製造装置で製造できたために、製造設備と製造工程とを簡略化して、パネルを製造できた。この第３の実施例では、赤、緑、青の３種類の蛍光体薄膜をストライプ状に加工して、並列に配置した多色表示薄膜ＥＬパネルを説明したが、複数の蛍光体薄膜を積み重ね、各蛍光体薄膜の上下に、絶縁膜と電極薄膜とを設けて、上記複数の蛍光体薄膜への個別の電圧印加が可能な構造にしても、多色表示薄膜ＥＬパネルが製造できる。また、赤、緑、青の３種類の蛍光体薄膜を順に積み重ねると、白色表示薄膜ＥＬパネルを製造することもできる。

【００３５】第３の実施例は、この発明の前記蛍光体薄膜を有する薄膜ＥＬパネルに関するものである。したがって、薄膜ＥＬパネルに、この発明の蛍光体薄膜が含まれておればよく、蛍光体薄膜の種類や数が制限されるものではない。例えば、従来の黄橙色ＺｎＳ：Ｍｎ蛍光体薄膜と、この発明の蛍光体薄膜を組み合わせても良いし、緑色Ｓｒ（Ｉｎ，Ｇａ）２Ｓ４：Ｅｕと、赤色ＳｒＩｎ$_2$ Ｓ$_4$ ：Ｅｕとの２種類の蛍光体薄膜だけを組み合わせても良い。組み合わせる、この発明の蛍光体薄膜の数はいくつであってもよい。蛍光体薄膜の発光色や組合せ方も、制限されるものではない。

【００３６】

【発明の効果】本発明によれば、ＡＢ２Ｃ４：Ｒｅの構造式（但し、ＡはＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素であり、ＢはＩｎおよびＡｌから選ばれた少なくとも１つの元素とＧａとを組み合わせた複合元素であり、ＣはＳおよびＳｅから選ばれた少なくとも一つの元素であり、Ｒｅは希土類の添加物を示す。）で表される化合物を主体にして蛍光体薄膜を構成するので、赤から青までの、広範囲にわたる多色ＥＬを示す蛍光体薄膜を提供することができる。

【００３７】また、本発明によれば、ＡＢ２Ｃ４：Ｒｅの構造式（但し、ＡはＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素であり、ＢはＩｎおよびＡｌから選ばれた少なくとも１つの元素であり、ＣはＳおよびＳｅから選ばれた少なくとも一つの元素であり、Ｒｅは希土類の添加物を示す。）で表される化合物を主体にして蛍光体薄膜を構成もするので、赤から青までの、広範囲にわたる多色ＥＬを示す蛍光体薄膜を提供することができる。とりわけ、ＳｒＩｎ$_2$ Ｓ$_4$ ：Ｅｕの構造式で表される化合物を主体にして蛍光体薄膜を構成すると、高輝度の赤色ＥＬを示す蛍光体薄膜を提供することができる。

【００３８】また、本発明によれば、上記ＡＢ２Ｃ４：Ｒｅの構造式（但し、ＡはＭｇ，Ｃａ，Ｓｒ，Ｂａ，ＥｕおよびＹｂから選ばれた少なくとも一つの元素であり、ＢはＩｎおよびＡｌから選ばれた少なくとも１つの元素とＧａとを組み合わせた複合元素、または、Ｉｎお

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よびＡｌから選ばれた少なくとも１つの元素であり、ＣはＳおよびＳｅから選ばれた少なくとも一つの元素であり、Ｒｅは希土類の添加物を示す。）で表される化合物を主体にした蛍光体薄膜を用いて薄膜ＥＬパネルを構成するので、フィルタを用いなくとも赤から青までの、広範囲にわたる多色ＥＬを示す薄膜ＥＬパネルを提供することができる。とりわけ、ＳｒＩｎ2 Ｓ4：Ｅｕの構造式で表される化合物を主体にした蛍光体薄膜を用いて薄膜ＥＬパネルを構成すると、高輝度の赤色ＥＬを示す薄膜ＥＬパネルを提供することができる。

【図面の簡単な説明】

【図１】この発明の第１の実施例の蛍光体薄膜を用いた薄膜ＥＬパネルの構造図である。

【図２】この発明の第１の実施例の蛍光体薄膜の製造装置の概念図である。

【図３】蛍光体薄膜のＸ線回折パターンである。

【図４】蛍光体薄膜のＥＬ特性である。

【図５】蛍光体薄膜のＥＬスペクトルである。

【図６】この発明の第２の実施例の蛍光体薄膜の製造装置を示す概念図である。

【図７】この発明の第３の実施例の薄膜ＥＬパネルの断面図である。

【符号の説明】

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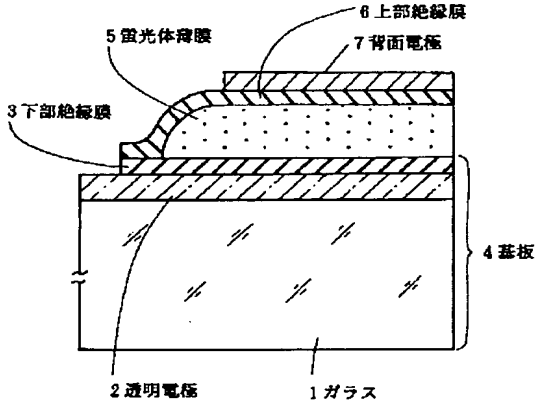
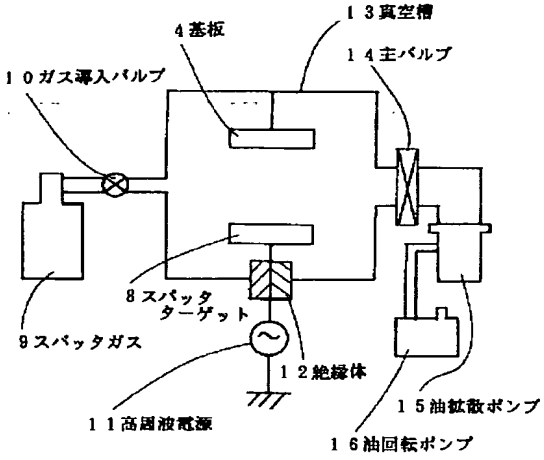
	１	ガラス
	２	透明電極
	３	下部絶縁膜
	４	基板
	５	蛍光体薄膜
	６	上部絶縁膜
	７	背面電極
	８	スパッタターゲット
	９	スパッタガス
10	１０	ガス導入バルブ
	１１	高周波電源
	１２	絶縁体
	１３	真空槽
	１４	主バルブ
	１５	油拡散ポンプ
	１６	油回転ポンプ
	１７	H_2 Ｓガスボンベ
	１８	Ｓｒ金属
	１９	Ｉｎ金属
20	２０	$EuCl_3$ 化合物粉末
	２１	赤色蛍光体薄膜
	２２	緑色蛍光体薄膜
	２３	青色蛍光体薄膜

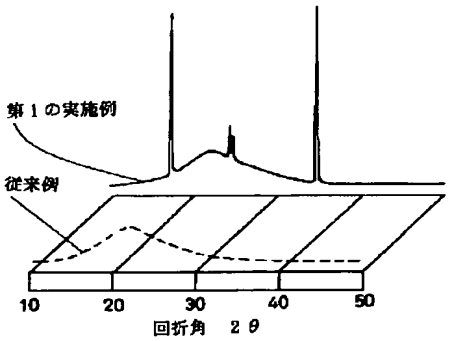
【図１】



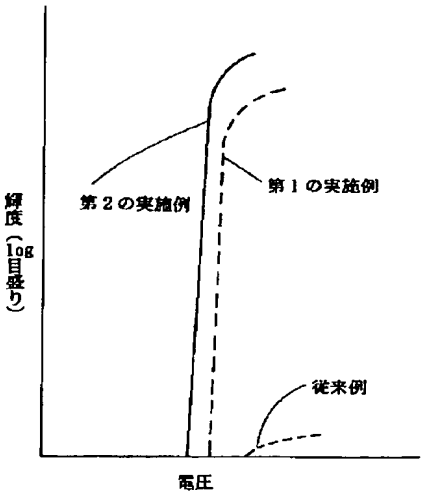
【図２】



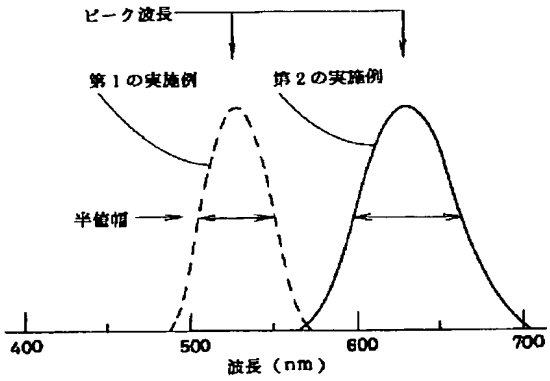
【図３】


第１の実施例
従来例
10
20
30
40
50
回折角　２θ

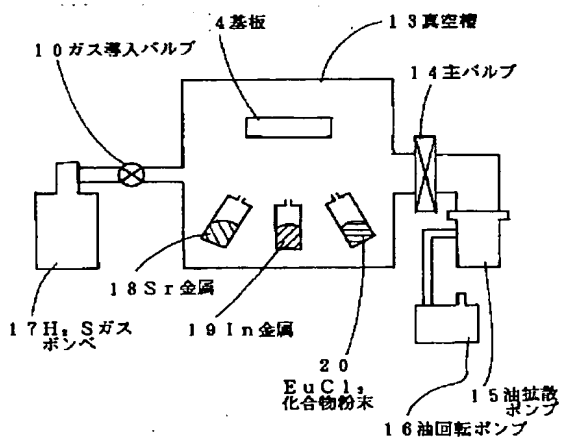
【図４】


第２の実施例
第１の実施例
従来例
輝度（log目盛り）
電圧

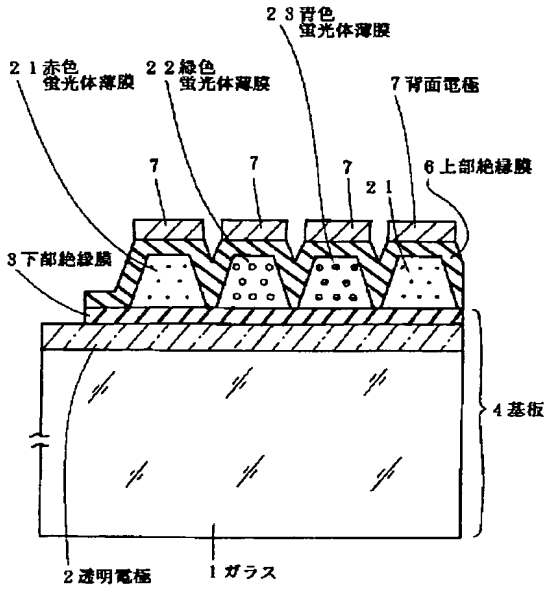
【図５】


ピーク波長
第１の実施例
第２の実施例
半値幅
400
500
600
700
波長（nm）

【図６】


４基板
１３真空槽
１０ガス導入バルブ
１４主バルブ
１８Ｓｒ金属
１７Ｈ₂Ｓガス
ボンベ
１９Ｉｎ金属
２０
ＥｕＣｌ₃
化合物粉末
１５油拡散
ポンプ
１６油回転ポンプ

【図７】



フロントページの続き

(58)調査した分野(Int.Cl.[6]，ＤＢ名)

H05B　33/14
C09K　11/00
G09F　9/30　　365

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] AB2 C4 : It is the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re. Said A is at least one element chosen from Mg, calcium, Sr, Ba, Eu, and Yb. The fluorescent substance thin film characterized by for said B being at least one element chosen from aluminum, Ga, and In, for said C being at least one element chosen from S and Se, and said Re being the additive of rare earth.
[Claim 2] AB2 C4 : It is the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re. Said A is at least one element chosen from Mg, calcium, Sr, Ba, Eu, and Yb. The fluorescent substance thin film characterized by for said B being at least one element chosen from aluminum and In, for said C being at least one element chosen from S and Se, and said Re being the additive of rare earth.
[Claim 3] The fluorescent substance thin film which is at least one element with which Re was chosen from Eu and Ce in the fluorescent substance thin film according to claim 2.
[Claim 4] AB2 C4 : Fluorescent substance thin film characterized by being the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re, said A being Sr, said B being In, said C being S, and said Re being Eu.
[Claim 5] The manufacture approach of the fluorescent substance thin film characterized by forming a fluorescent substance thin film by the reactant spatter which is the manufacture approach of a fluorescent substance thin film of manufacturing a fluorescent substance thin film according to claim 1, and contains the gas of the hydride which has the element which constitutes C in sputtering gas.
[Claim 6] The manufacture approach of the fluorescent substance thin film characterized by controlling independently two or more steamy gas which has one or more kinds of each element which is the manufacture approach of a fluorescent substance thin film of manufacturing a fluorescent substance thin film according to claim 1, and constitutes A, B, C, and Re, supplying it to a substrate front face, and forming a fluorescent substance thin film.
[Claim 7] The manufacture approach of the fluorescent substance thin film which supplies each metallic fumes which constitute A and B which were gasified according to the individual in the manufacture approach of a fluorescent substance thin film according to claim 6, the steam of the halogenide of gasified Re, and the gas of the hydride which has the element which constitutes C to a substrate front face, and forms a fluorescent substance thin film.
[Claim 8] The manufacture approach of the fluorescent substance thin film which gasifies each element which constitutes A, B, C, and Re according to an individual in the manufacture approach of a fluorescent substance thin film according to claim 6, supplies a substrate front face, and forms a fluorescent substance thin film.
[Claim 9] The manufacture approach of the fluorescent substance thin film which supplies A gasified according to the individual, the steam of each halogenide of B and Re, and the gas of the hydride which has the element which constitutes C to a substrate front face in the manufacture approach of a fluorescent substance thin film according to claim 6, and forms a fluorescent substance thin film.
[Claim 10] The manufacture approach of the fluorescent substance thin film which supplies two or more steamy gas to a substrate front face by turns, and forms a fluorescent substance thin film in the manufacture approach of a fluorescent substance thin film according to claim 6.
[Claim 11] The thin film EL panel which has two or more kinds of fluorescent substance thin films according to claim 1.
[Claim 12] It sets to a thin film EL panel according to claim 11, and two or more kinds of fluorescent substance thin films are SrIn2 S4. : Eu red fluorescent substance thin film and SrGa2 S4 : Eu green fluorescent substance thin film and SrGa2 S4 : Thin film EL panel which is Ce blue fluorescent substance thin film.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention excels [thin shape] in the visibility of a display, is the optimal as terminal displays, such as OA equipment, and relates to the fluorescent substance thin film and the manufacture approach of a thin film EL element applicable to a multicolor display thin film EL panel, and the thin film EL panel using it.
[0002]
[Description of the Prior Art] In recent years, rare earth elements, such as manganese, a terbium, samarium, a thulium, europium, and a cerium, are known as an element with which II-VI group compound semiconductors, such as zinc sulfide, calcium sulfide, a strontium sulfide, a zinc selenide, and selenium-ized strontium, serve as an emission center added into a parent ingredient again as a parent ingredient of the fluorescent substance thin film of a thin film EL element. In order to produce the EL panel which can be displayed full color also in a multicolor display thin film EL panel, it is necessary to obtain the red of high brightness and high color purity, green, and three kinds of blue luminescence from a fluorescent substance thin film. Red luminescence obtained by separating the red component of the yellow orange light from a ZnS:Mn fluorescent substance thin film using the red filter of CdSSe or an organic compound and green luminescence obtained by separating the green component of the yellow orange light from a ZnS:Mn fluorescent substance thin film using the green filter of an organic compound, and green luminescence from a ZnS:Tb fluorescent substance thin film are used for current and a multicolor display thin film EL panel. As blue luminescence, bluish green color luminescence of high brightness obtained from a SrS:Ce fluorescent substance thin film is known. Good blue luminescence of color purity can be obtained by combining with a blue filter.
[0003]
[Problem(s) to be Solved by the Invention] However, since the film production approaches for obtaining high brightness according to the class of fluorescent substance thin film since the chemical or physical property which the parent ingredient and emission center ingredient of a fluorescent substance have changes with each ingredients differed, there was a problem to which it becomes much more complicated and the manufacturing cost of a panel becomes high for the reasons nil why the production process of a multicolor thin film EL panel is [the film production equipment of offseeds] needed etc. for example, said ZnS:Mn fluorescent substance thin film -- resistance-wire heating vacuum deposition, electron beam vacuum deposition, and an atomic layer -- epitaxial (ALE) -- high brightness is obtained by producing a film using law. Moreover, high brightness is obtained when a ZnS:Tb fluorescent substance thin film produces a high frequency spatter and a SrS:Ce fluorescent substance thin film using electron beam vacuum deposition. In order to solve the above-mentioned problem, the fluorescent substance parent ingredient and emission center ingredient which become possible [obtaining high brightness using the same film production technique or film production equipment] and with which the chemical or physical property was similar were called for.
[0004] Moreover, when a multicolor thin film EL panel is produced using said conventional fluorescent substance thin film (ZnS:Mn, ZnS:Tb, SrS:Ce), in order to obtain luminescence of red, green, and blue The filter of CdSSe or an organic compound was needed in many cases, and there were a problem to which the production process of a multicolor thin film EL panel becomes more complicated, and a problem to which brightness falls to 10 - 60% of the brightness before transparency by penetrating a filter, and the image of a panel becomes dark. In order to solve the above-mentioned problem, even if it did not use a filter, the good red of color purity, green, and the fluorescent substance thin film that can obtain blue luminescence were called for.
[0005] This invention aims at obtaining the far-reaching multiple color EL in from red to blue which does not need a filter. Moreover, this invention simplifies the production process of a multicolor display thin film EL panel, and aims at reducing the manufacturing cost of a multicolor display thin film EL panel.

[0006]
[Means for Solving the Problem] The fluorescent substance thin film of this invention is AB2 C4. : It is the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re. A is at least one element chosen from Mg, calcium, Sr, Ba, Eu, and Yb. B is at least one element chosen from aluminum, Ga, and In, C is at least one element chosen from S and Se, and it is characterized by Re being the additive of rare earth.
[0007] The fluorescent substance thin film of this invention is produced by the reactant spatter which contains the gas of the hydride which has the element which constitutes C in sputtering gas, or the film production technique which controls independently two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re, supplies a substrate front face, and forms a thin film. Furthermore, a multicolor display thin film EL panel is manufactured using some kinds of fluorescent substance thin films of this invention.
[0008] the film production technique which controls independently two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re, supplies a substrate front face, and forms a thin film -- reactant vacuum deposition and molecular beam epitaxy (MBE) -- law and halogen transportation chemical vapor growth (CVD) -- law and the ALE method (another name: intermittent CVD method) are included. Reactant vacuum deposition supplies each metallic fumes which constitute A and B which were gasified according to the individual, the steam of the halogenide of gasified Re, and the gas of the hydride which has the element which constitutes C to a substrate front face, and forms a fluorescent substance thin film.
[0009] molecular beam epitaxy (MBE) -- law supplies each metallic fumes which constitute A and B which were gasified according to the individual, and C and Re to a substrate front face, and forms a fluorescent substance thin film. halogen transportation chemical vapor growth (CVD) -- law supplies A gasified according to the individual, the steam of each halogenide of B and Re, and the gas of the hydride which has the element which constitutes C to a substrate front face, and forms a fluorescent substance thin film.
[0010] The ALE method (another name: intermittent CVD method) supplies two or more steamy gas to a substrate front face by turns, and forms a fluorescent substance thin film.
[0011]
[Function] According to this invention, the far-reaching multiple color EL from red to blue which does not need a filter can be obtained. It is especially SrIn2 S4. : Eu fluorescent substance thin film is high brightness red luminescence with good color purity SrGa2 S4 : Eu fluorescent substance thin film can realize high brightness green luminescence with good color purity. In a compound, the rare earth which is an additive exists as rare earth ion, and works as an emission center. In this case, the luminescent color resulting from the energy which 4 f electrons which rare earth ion has have is obtained. The content of the rare earth elements from which the value of an addition x becomes 0.001 to 0.1, i.e., an emission center, has desirable 0.1 - 10 atom %.
[0012] Furthermore, the reactant spatter which contains the gas of the hydride which has the element which constitutes C in sputtering gas, Or by forming a fluorescent substance thin film by the film production technique which controls independently two or more steamy gas which has one or more kinds of each metallic element which constitutes A, B, C, and Re, and is supplied to a substrate front face By being able to produce the fluorescent substance thin film of varieties with the same film production equipment, and using a multicolor display thin film EL panel as the panel which has the fluorescent substance thin film of offseeds, the production process of a multicolor display thin film EL panel can be simplified, and the manufacturing cost of a multicolor display thin film EL panel can be reduced.
[0013]
[Example] (The 1st example) Below, it explains, referring to a drawing about the 1st example of this invention. Drawing 1 is the sectional view of the thin film EL element which can apply this invention. On glass 1, the sequential deposition of the transparent electrode 2 of the indium oxide (ITO) which added tin, and the lower insulator layer 3 of acid silicon nitride (SiON) was carried out using the RF spatter, and it considered as the substrate 4 for EL elements. On the substrate 4, 600-800nm of fluorescent substance thin films 5 was formed. After using the up insulator layer 6 of tantalic acid barium (BaTa2 Ox;x are about 6) and making a RF spatter deposit on the fluorescent substance thin film 5, the back plate 7 of aluminum (aluminum) was deposited with electron ray heating vacuum deposition, and it considered as the thin film EL element. Alternating voltage with a frequency of 1kHz was impressed between the transparent electrode 2 of ITO, and the back plate 7 of aluminum, and the thin film EL element was driven.
[0014] Hereafter, the manufacture approach of the fluorescent substance thin film of the 1st example is explained. The fluorescent substance thin film of this 1st example is SrGa2 S4 whose rare earth elements used as an emission center are Eu. : It is Eu fluorescent substance thin film. Drawing 2 is the conceptual diagram of the RF sputtering system which is a manufacturing installation of the fluorescent substance thin film of this 1st example.
[0015] As a spatter target 8, it is SrGa2 S4. : Eu fluorescent substance powder was used. The addition of Eu which is the

additive of the rare earth used as an emission center was made into pentatomic %, x= 0.05 [i.e.,]. Ar+5%H2 S mixed gas was made into sputtering gas 9. 10 -- a gas installation bulb and 11 -- an RF generator and 12 -- an insulator and 13 -- a vacuum tub and 14 -- a main valve and 15 -- an oil diffusion pump and 16 -- an oil sealed rotary pump -- it comes out. The substrate temperature of 300-600 degrees C, 5Pa of gas pressure, and RF power-flux-density 3.8 W/cm2 A sputtering rate and about 10 nm/min were obtained under spatter conditions. SrGa2 S4 which shows EL property which was excellent under the above-mentioned spatter conditions by performing 650-degree-C heat treatment of 1 hour in a vacuum after manufacturing the thin film which consists of Sr-Eu-Ga-S on a substrate 4 : Eu fluorescent substance thin film was able to be manufactured.

[0016] Drawing 3 is drawing showing the X diffraction pattern of a fluorescent substance thin film. For the comparison, the X diffraction pattern of the thin film which produced sputtering gas as Ar was also shown in this drawing as a conventional example. Several peaks were able to be accepted in the X diffraction pattern by replacing with a spatter from the former whose sputtering gas is Ar gas, and considering as the reactant spatter which makes sputtering gas the Ar+H2 S mixed gas which contains H2 S which has S, and which is gas of a hydride in 5% sputtering gas in this 1st example. This shows that the crystallized thin film is obtained by the manufacture approach of the fluorescent substance thin film of this 1st example, and shows that the fluorescent substance thin film parent of high performance has been manufactured by considering as the reactant spatter which makes Ar+H2 S mixed gas sputtering gas in more detail.

[0017] Drawing 4 is drawing showing the EL property of a fluorescent substance thin film. Change of the brightness to an electrical potential difference is shown. For the comparison, the EL property of the thin film which produced sputtering gas as Ar was also shown in this drawing as a conventional example. The EL property of the 2nd example shown in drawing 4 is explained later. High EL brightness was able to be obtained by replacing with a spatter from the former whose sputtering gas is Ar gas, and considering as the reactant spatter which makes sputtering gas the Ar+H2 S mixed gas which contains H2 S which has S, and which is gas of a hydride in 5% sputtering gas in this 1st example. This shows that the fluorescent substance thin film of high performance has been manufactured by the manufacture approach of the fluorescent substance thin film of this 1st example. It is thought that H2 S in sputtering gas bears the role which prevents the reevaporation of S component from a fluorescent substance thin film to the midst a fluorescent substance thin film grows up to be.

[0018] Drawing 5 is drawing showing EL spectrum of a fluorescent substance thin film. EL spectrum of the 2nd example is explained later. The peak wavelength of luminescence was about 526nm, and the half-value width of a spectrum was about 47nm. For this, the fluorescent substance thin film manufactured by the manufacture approach of the fluorescent substance thin film of this 1st example is SrGa2 S4 which shows green luminescence. : It is shown that it is Eu fluorescent substance thin film.

[0019] It is SrGa2 S4 as explained above. : It is SrGa2 S4 of high performance by forming by the reactant spatter which contains the H2 S gas which is the hydride which has S for the fluorescent substance thin film expressed with the structure expression of Eu in sputtering gas. : Eu fluorescent substance thin film could be manufactured and the thin film EL of high brightness was able to be obtained. At this 1st example, it is a fluorescent substance thin film material Green luminescence SrGa2 S4 : Although the case where it considered as Eu fluorescent substance was explained SrGa2 S4 which it replaced with Sr, and replaced with Eu rare earth elements, and it was referred to as Mg, calcium, Ba, Eu, and Yb, or was set [, and / replaced with Ga and] to aluminum or In : The thin film EL was observable with fluorescent substance thin films other than Eu. [considering as rare earth elements, such as Ce and Pr,] In the additive of rare earth, Eu and Ce show high brightness, and they are division and red luminescence SrIn2 S4. : Eu, green luminescence SrGa2 S4 : In the case of Eu fluorescent substance thin film, the high brightness EL was able to be obtained. Moreover, SrGa2 S4 : Ce and BaAl2 S4 : In the case of Eu fluorescent substance thin film, the blue EL light emitting device excellent in color purity was able to be obtained.

[0020] As explained above, it is AB2 C4. : The thin film EL ranging from the fluorescent substance thin film to the visible region whole region which makes a subject the compound expressed with the structure expression of Re was realizable. In addition, AB2 C4 : In the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re, A, B, C, and Re are not limited to a single element. For example, 2 (Ga(Sr1-x Cax) 1-y Iny) 4 (S1-z Sez) : It is good as for plurality like Eu and Ce in the element which constitutes A, B, and C, and it cannot be overemphasized that offseed addition of the rare earth elements may be carried out.

[0021] Moreover, it is green luminescence SrGa2 S4 by the reactant spatter which made Ar+H2 S mixed gas sputtering gas in this example. : Although the case where Eu fluorescent substance thin film was produced was explained For example, SrGa2 Se4 : In the case of Eu fluorescent substance thin film Ar+H2 Se mixed gas is made into sputtering gas, and it is SrGa2 Se4 about a spatter target. : By the reactant spatter used as Eu fluorescent substance powder The fluorescent substance thin film in which the high brightness EL is shown is caused by film production, and it is SrGa2 4

(S1-x Sex). : In the case of Eu fluorescent substance thin film Ar+H2 Se mixed gas is made into sputtering gas, and it is a spatter target SrGa2 S4 : The film has been produced by the reactant spatter used as Eu fluorescent substance powder.
[0022] Furthermore, at this 1st example, it is green luminescence SrGa2 S4. : Although the case where Eu fluorescent substance powder was used as a spatter target was explained, even if it replaced with the powder target and used the ceramics target, the fluorescent substance thin film in which the same outstanding EL property as the case of a powder target is shown was able to be obtained. The ceramics target has produced the fluorescent substance thin film with more sufficient repeatability.
[0023] This 1st example is AB2 C4. : In the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re, it is also characterized by forming a fluorescent substance thin film by the reactant spatter which contains the gas of the hydride which has the element which constitutes C in sputtering gas. Therefore, it is not restricted about the class of the gestalt of a spatter target, a configuration and the amount of mixing of gas, or gas that the gas of the hydride which has the element which constitutes C should just be contained in sputtering gas. For example, the amount of mixing of the gas of the hydride which has the element which may replace with Ar+H2 S mixed gas, may use the mixed gas of the gas of the offseeds like Ar+helium+H2 S+H2 Se mixed gas, and constitutes C may not be 5%.
[0024] (The 2nd example) Next, it is AB2 C4. : In the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re, the manufacture approach of the fluorescent substance thin film which controls independently two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re, and supplies it to a substrate front face is explained. That is, the additive of the rare earth used as the emission center which is the 2nd example is red luminescence SrIn2 S4 of Eu. : The manufacture approach of Eu fluorescent substance thin film is explained.
[0025] Drawing 6 is the conceptual diagram of the manufacturing installation of the fluorescent substance thin film of this 2nd example. EuCl3 which are Sr metallic-fumes gas and the halogenide of Eu respectively about two or more steamy gas which has each metallic element which constitutes A, B, C, and Re The fluorescent substance thin film of the 2nd example is manufactured with the reactant vacuum deposition made into compound steamy gas, In metallic-fumes gas, and H2 S gas.
[0026] In drawing 6 , the substrate 4 installed in the high vacuum tub 13 was first heated at 600 degrees C, and high vacuum equipment was exhausted to 1x10 - 6 or less Pa. In order to supply H2 S of the specified quantity to the front face of a substrate 4, the gas installation bulb 10 was operated so that it might become the pressure of 1x10 to 2 Pa, and H2 S gas was introduced in high vacuum equipment from the H2 S chemical cylinder 17. The Sr metal 18 installed into the vacuum next, the In metal 19, and EuCl3 The compound powder 20 was heated and gasified according to the individual, and the front face of a substrate 4 was supplied. They are 400-900 degrees C and EuCl3 about 500-600 degrees C and In metal in Sr metal. By keeping compound powder at 500-800 degrees C, the thin film which consists of Sr-Eu-In-S was manufactured. Red luminescence SrIn2 S4 which shows EL property which was excellent by performing 650-degree-C heat treatment of 1 hour in a vacuum after thin film formation : Eu fluorescent substance thin film was able to be manufactured.
[0027] SrIn2 S4 of the 2nd example : The EL property of Eu fluorescent substance thin film is shown in drawing 4 . Green luminescence SrGa2 S4 of the 1st example which produced the film by the reactant spatter : Although it was shown in drawing 4 in order to compare with the case of Eu fluorescent substance thin film, it turns out that high EL brightness is realizable with this reactant vacuum deposition. EL spectrum of the fluorescent substance thin film of the 2nd example is shown in drawing 5 . Green luminescence SrGa2 S4 of the 1st example which produced the film by the reactant spatter : In order to compare with the case of Eu fluorescent substance thin film, it was shown in drawing 5 . The peak wavelength of luminescence was about 630nm, and the half-value width of a spectrum was about 65nm. This shows that the fluorescent substance thin film of the 2nd example manufactured by the manufacture approach of this fluorescent substance thin film is a SrIn2 S4:Eu fluorescent substance thin film in which red luminescence is shown.
[0028] It is SrIn2 S4 as explained above. : The fluorescent substance thin film expressed with the structure expression of Eu Sr metallic-fumes gas and EuCl3 By forming with the reactant vacuum deposition which controls independently compound steamy gas, In metallic-fumes gas, and H2 S gas, supplies a substrate front face, and forms a fluorescent substance thin film SrIn2 S4 of high performance : Eu fluorescent substance thin film could be manufactured and the thin film EL of high brightness was able to be obtained.
[0029] It is two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re from this 2nd example respectively Sr metallic-fumes gas and EuCl3 Although the case where a substrate front face was supplied as compound steamy gas, In metallic-fumes gas, and H2 S gas was explained Even if it supplies the sulfur which made solid-state sulfur heat and gasify instead of H2 S gas The fluorescent substance thin film of the outstanding

quality which is not different from the time of using hydrogen-sulfide gas was able to be formed, and it is EuCl3. Even if it made Metal Eu heat and gasify instead of compound powder, the fluorescent substance thin film was able to be formed. Moreover, it is SrCl2 instead of Sr metal. Even if it made compound powder heat and gasify, the fluorescent substance thin film was able to be formed, and it is InCl3 instead of In metal. Even if it made compound powder heat and gasify, the fluorescent substance thin film was able to be formed.

[0030] MBE which supplies each metallic fumes which constitute A and B by which this was gasified according to the individual, and C and Re to a substrate front face -- with law, and A and the steam of the halogenide of B and Re gasified according to the individual It is shown also by the ALE method (another name: intermittent CVD method) which supplies the gas of the hydride which has the element which constitutes C to a substrate front face and which supplies a halogen transportation CVD method and further two or more steamy gas to a substrate front face by turns that a fluorescent substance thin film can be manufactured.

[0031] Moreover, it is two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re from this 2nd example respectively Sr metallic-fumes gas and EuCl3 As compound steamy gas, In metallic-fumes gas, and H2 S gas Red luminescence SrIn2 S4 : It is green luminescence SrGa2 S4 by replacing with In metallic-fumes gas and supplying Ga metallic-fumes gas to a substrate front face, although the case where Eu fluorescent substance thin film was produced was explained. : Eu fluorescent substance thin film has been produced. Moreover, Sr metallic-fumes gas and CeCl3 It is blue luminescence SrGa2 S4 by controlling compound steamy gas, Ga metallic-fumes gas, and H2 S gas, and supplying a substrate front face. : Ce fluorescent substance thin film has also been produced.

[0032] According to the manufacture approach of the fluorescent substance thin film this invention, this shows that the fluorescent substance thin film of this invention covering varieties can produce a film, also shows that red, green, and the fluorescent substance thin film of this blue invention can produce a film with one equipment, and shows that the multicolor display thin film EL panel of low cost can be manufactured. This invention relates to the manufacture approach of the fluorescent substance thin film characterized by controlling independently two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re, and supplying it to a substrate front face. Therefore, it is not restricted about the supply approach of the class of each steamy gas, or gas that two or more steamy gas which has one or more kinds of each element which constitutes A, B, C, and Re is controlled independently, is supplied to a substrate front face, and the fluorescent substance thin film should just be manufactured. The ambient pressure force at the time of supplying steamy gas is not restricted, either.

[0033] (The 3rd example) Next, it is AB2 C4. : The thin film EL panel which has the fluorescent substance thin film which makes a subject the compound expressed with the structure expression of Re offseeds is explained. As the 3rd example, it is red SrIn2 S4. : Eu, green SrGa2 S4 : Eu, blue SrGa2 S4 : The multicolor display thin film EL panel which has Ce fluorescent substance thin film is shown in drawing 7 . In drawing 7 , the red fluorescent substance thin film 21 processed in the shape of a stripe, the green fluorescent substance thin film 22, and the blue fluorescent substance thin film 23 are arranged to juxtaposition on a substrate 4.

[0034] Since the transparent electrode 2 and the lower insulating layer 3 were transparent, luminescence of the red from a fluorescent substance thin film, green, and blue was able to be guessed the direct view through glass 1. Since the filter is not used, and since it manufactured by the manufacturing installation with the same fluorescent substance thin film, the manufacturing facility and the production process were simplified and the panel has been manufactured. Although this 3rd example explained the multicolor display thin film EL panel which processed red, green, and three kinds of blue fluorescent substance thin films in the shape of a stripe, and has been arranged to juxtaposition, two or more fluorescent substance thin films are accumulated, and even if it prepares an insulator layer and an electrode thin film in the upper and lower sides of each fluorescent substance thin film and makes it the structure in which the electrical-potential-difference impression according to individual to two or more above-mentioned fluorescent substance thin films is possible, a multicolor display thin film EL panel can be manufactured. Moreover, if red, green, and three kinds of blue fluorescent substance thin films are accumulated in order, a white display thin film EL panel can also be manufactured.

[0035] This invention relates said fluorescent substance thin film of this invention to the thin film EL panel which it has offseeds. Therefore, the class or number of fluorescent substance thin films are not restricted for the fluorescent substance thin film of this invention to a thin film EL panel offseeds that what is necessary is to just be contained. For example, the conventional yellow orange ZnS:Mn fluorescent substance thin film and green SrGa2 S4 of this invention : Eu and green SrGa2 S4 : Three kinds of fluorescent substance thin films with Eu may be combined, and it is green SrGa2 S4. : Eu and red SrIn2 S4 : Only two kinds of fluorescent substance thin films with Eu may be combined. The number of the fluorescent substance thin films of this invention to combine may be four or more. Neither the luminescent color of a fluorescent substance thin film nor the method of combination is also restricted.

[0036]
[Effect of the Invention] Even if it does not use a filter according to this invention, it is possible to obtain the far-reaching multiple color EL from red to blue, while being able to manufacture the multicolor thin film EL element which is excellent in display quality, the high brightness fluorescent substance thin film of varieties can be produced with the same film production equipment, low-cost-izing of a multicolor display thin film EL panel is also possible, and practical value is large.

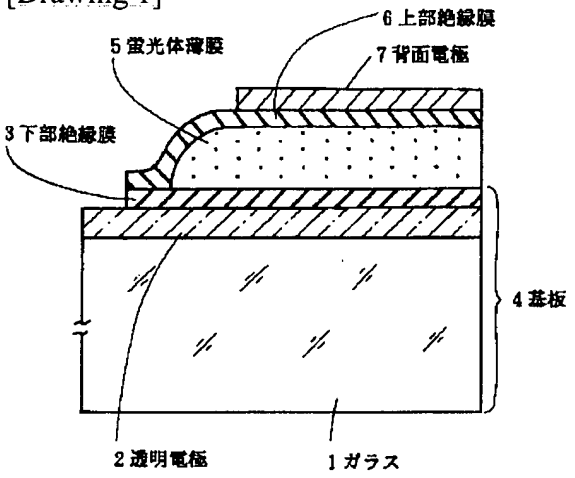
[Translation done.]

* NOTICES *

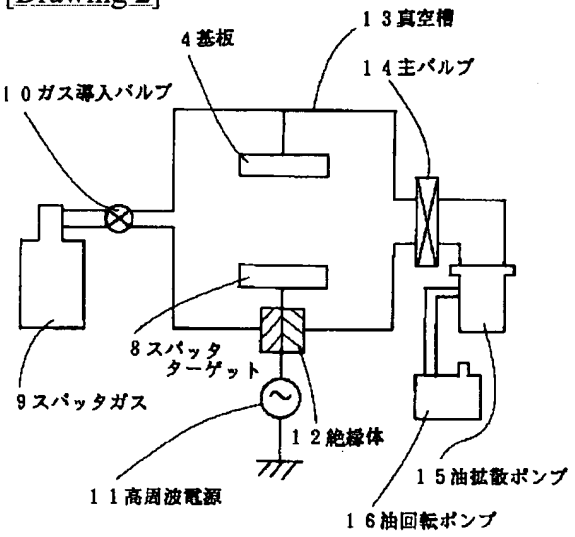
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

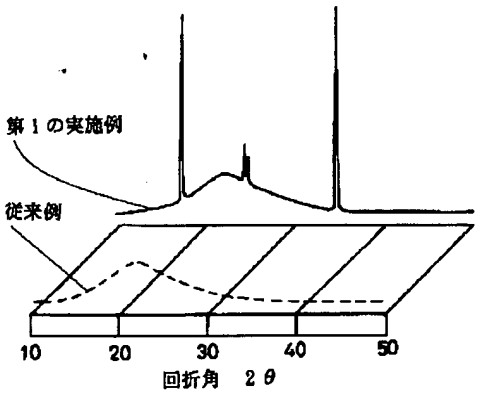
[Drawing 1]



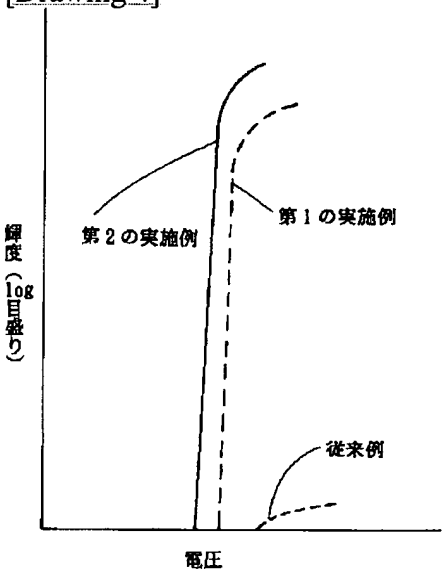
[Drawing 2]



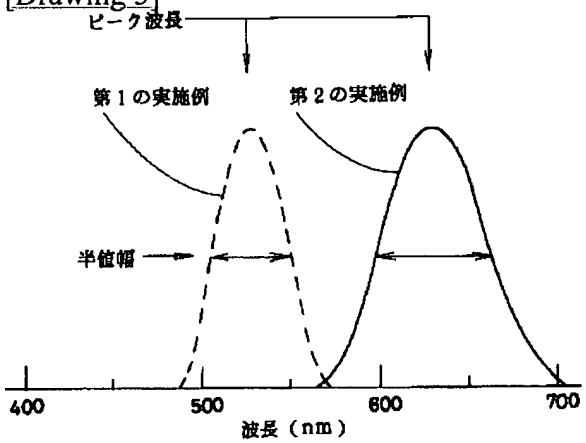
[Drawing 3]



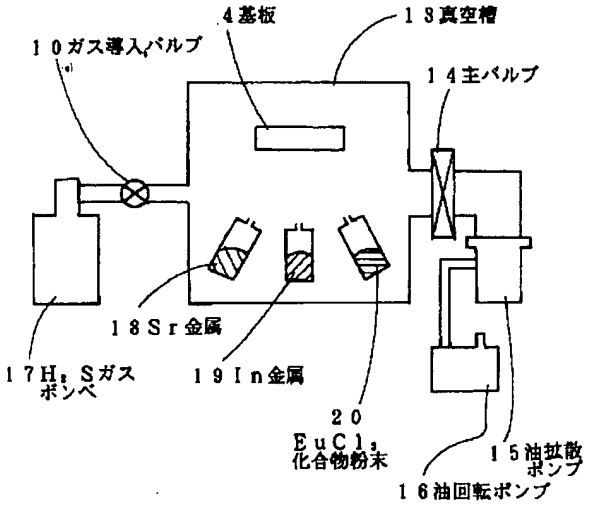
[Drawing 4]



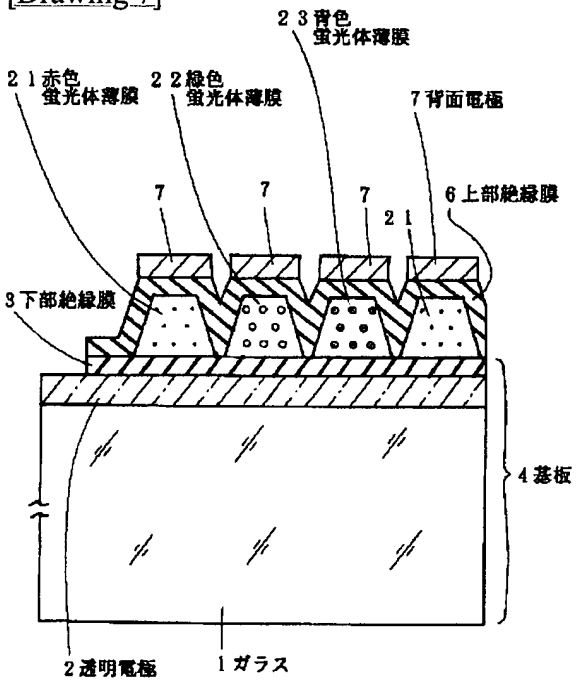
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]